



Research paper

Binuclear cyclopentadienylmetal carbonyl hydrides of iridium, osmium, and rhenium: The effect of electron count on the preferred structures

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ABSTRACT

The $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir, Os, Re}; n = 3, 2, 1$) systems, related to the experimentally known and structurally characterized permethylated derivatives $\text{Cp}^*_2\text{M}_2\text{H}_2(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$; $\text{M} = \text{Ir, Os}$), provide examples of binuclear structures having metal–metal bonds of formal orders ranging from zero to four as determined by the 18-electron rule. The low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures lacking a direct iridium–iridium bond necessarily have a bridging CO group holding together the two iridium atoms. For $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$, low-energy unbridged structures are found corresponding to the experimental unbridged $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure. However, for $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ the lowest energy structure has two hydrogen atoms bridging the formal Os=Os double bond similar to the experimental doubly bridged $\text{Cp}^*_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure. The lowest energy structures of the monocarbonyls $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})$ have all three ligands ($2\text{H} + \text{CO}$) bridging a central metal–metal bond. The $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures provide examples of both bridged and unbridged structures containing formal Re–Re quadruple bonds with highly bridged structures being preferred energetically.

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1. Introduction

Hydrides of the third row transition metals are found to be more stable and correspondingly less reactive than those of the first and second row transition metals. For example, rhenium forms the unusual stable binary nonacoordinate anion ReH_9^{2-} [1,2]. Stable cyclopentadienylmetal polyhydrides of the third row transition metals include the mononuclear derivatives Cp^*MH_n ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$; $\text{M} = \text{Re}$ [3,4], $n = 6$; $\text{M} = \text{Os}$ [5], $n = 5$; $\text{M} = \text{Ir}$ [6], $n = 4$). All of these mononuclear metal hydride derivatives obey the 18-electron rule [7–11]. The stable binuclear derivatives $\text{Cp}^*_2\text{M}_2\text{H}_n$ ($\text{M} = \text{Re}$ [3,4], $n = 6$; $\text{M} = \text{Os}$ [5], $n = 4$; $\text{M} = \text{Ir}$ [12], $n = 2$) also obey the 18-electron rule if the central $\text{M}\equiv\text{M}$ bond is regarded as a formal triple bond. In addition the mononuclear cyclopentadienylmetal carbonyl hydrides $\text{CpW}(\text{CO})_3\text{H}$ [13], $\text{CpRe}(\text{CO})_2\text{H}_2$ [14], $\text{CpOs}(\text{CO})_2\text{H}$ [15], and $\text{Cp}^*\text{Os}(\text{CO})\text{H}_3$ [16] are all isolable compounds, which are more stable and thus correspondingly less reactive than their analogues containing first and second row transition metals.

Two binuclear cyclopentadienylmetal carbonyl hydrides are known containing the third row transition metals, namely $\text{Cp}^*_2\text{Os}_2(\text{CO})_2\text{H}_2$ [16] and $\text{Cp}^*_2\text{Ir}_2(\text{CO})_2\text{H}_2$ [17]. Of interest are the same

molecular formulas for both species even though osmium has eight valence electrons and iridium has nine valence electrons. The structures of both species have been partially determined by X-ray crystallography but the hydrogen atoms could not be located. In order to clarify the nature of these species and related binuclear cyclopentadienylmetal carbonyl hydrides, the structures and thermochemistry of the complete series of $\text{Cp}_2\text{M}_2(\text{CO})_n\text{H}_2$ ($\text{M} = \text{Re, Os, Ir}; n = 3, 2, 1$) have been investigated using density functional theory. The metal–metal interactions in these binuclear cyclopentadienylmetal carbonyl hydrides are of particular interest since species with formal metal–metal bond orders ranging from 0 to 4 are found.

2. Theoretical methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have been regarded as a practical and effective computational tool, especially for organometallic compounds [18–24]. In our study, three DFT methods were used, namely BP86, MPW1PW91, and M06-L. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B) with Perdew's 1986 gradient-corrected correlation functional (P86) [25,26]. The MPW1PW91 method combines the modified Perdew-Wang exchange functional with the Perdew-Wang 91 gradient-correlation functional [27]. The M06-L method

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developed by Zhao and Truhlar [28] is based on the M05 [29] and VSXC [30] functionals. The MPW1PW91 functional is better than the first-generation functionals for second- and third-row transition metal systems [31], whereas the BP86 method provides more accurate vibrational frequencies [32,33]. In addition, a recent detailed study of 35 different DFT methods suggests that the M06-L method coupled with suitable basis sets predicts structures very consistent with experiment for transition metal organometallic and carbonyl derivatives [34]. For this reason, only the M06-L results (geometries, energies, and interatomic distances) are discussed in the text unless specifically noted otherwise.

The geometries of the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Re}, \text{Os}, \text{Ir}; n = 3, 2, 1$) structures were fully optimized using the three selected DFT methods with DZP and SDD basis sets for the light atoms and heavy atoms, respectively. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. Our DZP basis sets used for carbon, oxygen, and hydrogen add one set of pure spherical harmonic d functions with orbital exponents $R_d(\text{C}) = 0.75$, $R_d(\text{O}) = 0.85$, and $R_d(\text{H}) = 0.70$ to the standard Huzinaga-Dunning-Hay contracted DZ sets [35,36]. The carbon and oxygen basis sets are designated as (9s5p1d/4s2p1d), whereas the hydrogen basis set is designated as (4s1p/2s1p). The Stuttgart-Dresden double- ζ (SDD) effective core potential (ECP) basis set was used for the rhenium, osmium, and iridium atoms [37,38].

All of the computations were carried out using the Gaussian 09 program package [39]. A large number of stable structures were predicted by these three methods. If not specifically mentioned, only those structures with energies within ~ 10 kcal·mol⁻¹ by the M06-L method are discussed in the text. A summary of the vibrational frequencies and structure data calculated by M06-L, MPW1PW91 and BP86 method is given in the [Supporting Information](#).

3. Results

All of the structures discussed in this section have two pentahapto $\eta^5\text{-Cp}$ rings bonded to the metal atom and are genuine minima without any imaginary vibrational frequencies. The structures are ordered based on the energies predicted by the M06-L method.

3.1. The $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures

3.1.1. $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$

Seven low-energy structures were found for $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ (Fig. 1). Five of these seven structures, namely **Ir-3CO-2S** through **Ir-3CO-6S**, are related structures having non-bonding Ir–Ir distances ranging from 3.63 to 3.76 Å and closely spaced energies ranging from 1.2 to 3.9 kcal·mol⁻¹ above **Ir-3CO-1S**. Thus the two halves of each of these five molecules are held together solely by the bridging CO group. All five structures have one terminal hydrogen atom and one terminal CO group on each metal atom and differ only in the relative locations of the ligands.

The remaining two low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures **Ir-3CO-1S** and **Ir-3CO-7S** are geometrically quite different from the five structures **Ir-3CO-2S** through **Ir-3CO-6S**. Structure **Ir-3CO-1S** is the lowest energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structure. In **Ir-3CO-1S** one iridium atom bears a terminal CO group and a terminal hydrogen atom whereas the other iridium atom bears a terminal CO group and a terminal formyl group. Structure **Ir-3CO-7S**, lying 9.5 kcal·mol⁻¹ in energy above **Ir-3CO-1S**, is unusual since one of the Cp rings has “slipped” to become a trihapto ligand rather than the usual pentahapto ligand. The iridium atom bearing the trihapto Cp ring in **Ir-3CO-7S** is bonded to terminal CO groups whereas the other

iridium atom is bonded to a terminal hydrogen atom. The third CO group in **Ir-3CO-7S** bridges the two metal atoms. The Ir–Ir distances of ~ 2.8 Å in **Ir-3CO-1S** and **Ir-3CO-7S** can correspond to the formal single bonds required to give each iridium atom the favored 18-electron configuration.

3.1.2. $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$

Nine low-energy singlet $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structures having energies within 9 kcal·mol⁻¹ were optimized (Fig. 2). The Ir–Ir distances in all nine structures are predicted to range from 2.70 to 2.85 Å, consistent with formal single bonds. The global minimum **Ir-2CO-1S** is a C_2 *trans* structure with no bridging CO groups or hydrogen atoms. However, the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure very close to the experimental $\text{Cp}_2^*\text{Ir}_2\text{H}_2(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$) structure, characterized by X-ray crystallography, is **Ir-2CO-2S**, lying only 0.3 kcal·mol⁻¹ in energy above **Ir-2CO-1S** (Table 1) [17]. Thus, the predicted Ir–Ir distance in **Ir-2CO-2S** of 2.779 Å (M06-L), 2.740 Å (MPW1PW91), or 2.769 Å (BP86) is close to the Ir–Ir distance of 2.730 Å for $\text{Cp}_2^*\text{Ir}_2\text{H}_2(\text{CO})_2$ as determined by X-ray crystallography. The predicted Ir–C distances to the terminal CO groups in **Ir-2CO-2S** of 1.834 Å (M06-L), 1.826 Å (MPW1PW91), or 1.833 Å (BP86) are close to the experimental values of 1.817 and 1.829 Å for the two Ir–C bonds in $\text{Cp}_2^*\text{Ir}_2\text{H}_2(\text{CO})_2$. The predicted Ir–Ir–C bond angles of 85.8° (M06-L) or 86.6° (MPW1PW91) or 87.7° (BP86) are close to the experimental values of 85.1° and 85.4° for $\text{Cp}_2^*\text{Ir}_2\text{H}_2(\text{CO})_2$. The $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structures **Ir-2CO-2S** and **Ir-2CO-3S**, lying 0.3 and 2.1 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, are similar to **Ir-2CO-1S** and to each other except for the diverse dihedrals and angles. Thus the C–Ir–Ir–C dihedral angles in **Ir-2CO-1S**, **Ir-2CO-2S**, and **Ir-2CO-3S** are 96.6°, 180°, and 92.3°, respectively.

The next $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure **Ir-2CO-4S**, lying only 4.1 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, is a C_{2h} singlet structure with two hydrogen bridges and a terminal CO group on each iridium atom with a *trans* orientation of the two CO groups. Structure **Ir-2CO-8S**, lying 6.9 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, is the *cis* isomer corresponding to **Ir-2CO-4S**. Structure **Ir-2CO-5S**, lying 4.7 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, has the opposite ligand configuration of **Ir-2CO-8S** with two bridging CO groups and two terminal hydrogen atoms in a *cis* configuration. Structure **Ir-2CO-9S**, lying 8.8 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, is the *trans* isomer corresponding to **Ir-2CO-5S**. Structure **Ir-2CO-6S**, lying 6.3 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, has one bridging CO group. In **Ir-2CO-6S** two terminal hydrogen atoms are bonded to one of the iridium atoms and one terminal CO group is bonded to the other iridium atom.

The final low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure **Ir-2CO-7S**, lying 6.4 kcal·mol⁻¹ in energy above **Ir-2CO-1S**, is a doubly bridged structure with a bridging CO group and a bridging hydrogen atom. One iridium atom bears a terminal hydrogen atom whereas the other iridium atom bears a terminal CO group with the terminal ligands in a *trans* configuration. The hydrogen bridge is slightly unsymmetrical with Ir–H distances of 1.76 and 1.80 Å. The bridging CO group is considerably more unsymmetrical with Ir–C distances of 1.92 and 2.21 Å, respectively. The Ir–Ir distance in **Ir-2CO-7S** of 2.807 Å (M06-L) corresponds to a formal single bond, thereby giving each iridium atom the favored 18-electron configuration.

3.1.2. $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$

Six singlet $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures (Fig. 3) were optimized. The Ir–Ir distances in these $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures are predicted to range from ~ 2.50 to 2.62 Å, consistent with Ir=Ir double bonds. The lowest energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structure is a triply bridged C_{2v} structure **Ir-1CO-1S** with one bridging carbonyl group, two bridging hydrogen atoms with Ir–H distances of 1.799 Å, and cyclopentadienyl rings as the only terminal group bonded to each iridium

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